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A - 5

Genetic Problems of Some Sedimentary Manganese Carbonate Ores

by

P. A. MOHR

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Abstract

It is suggested on the basis of detailed geochemical studies that the manganese carbonate sediments of basal Middle Cambrian age in the Acadian and Welsh geosynclines (considered to be a single unit prior to continental drifting) owed their origin to the coincidence of three essential factors: the presence of penecontemporaneous spilitic and keratophyric lavas at source, the severe weathering conditions operating temporarily at source, and the existence of isolated basins of marine water in which the manganese salts could be concentrated and precipitated.

The stagnant marine waters of the basal Middle Cambrian basins of S.E. Newfoundland and Harlech-St. Tudwal's were warm, highly saline, alkaline and probably saturated with carbon dioxide. Silica, aluminium hydroxide and manganous carbonate were precipitated and flocculated under these conditions, the abundance of carbon dioxide and a rather low Eh preventing significant oxidation of the manganous ion. Cyclical banding, reflecting long-term climatic changes on land, was caused by variations of Eh-pH of the waters of the basin which thus notably affected the ferric/ferrous iron ratios in the precipitates. The presence of manganese oxide in the black bands of the Welsh Manganese Ore (corresponding to the green bands of the Newfoundland manganese bed) is not explicable solely in terms of Eh-pH, however.

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GENETIC PROBLEMS OF SOME SEDIMENTARY MANGANESE CARBONATE ORES

The Middle Cambrian manganese carbonate rocks of Newfoundland and Wales: the source and conditions of precipitation of the manganese.

by P.A. Mohr

1. INTRODUCTION

The writer has been concerned for some time with the geochemistry of the manganese beds and associated rocks of the Harlech Dome and St. Tudwal's regions in North Wales. Arising out of this detailed quantitative work (Mohr 1956, 1959, 1960, 1962, 1963, 1964 and Mohr & Allen 1965) there is now the need for a more general and qualitative synthesis concerning the position and nature of the source of the manganese, and the conditions under which it was precipitated at high concentration. Solutions to these problems were hinted at in a recent work (Mohr 1964), but a fuller treatment has been reserved for the present paper where it is shown that a more elegant palaeogeographical reconstruction is made possible by postulating that Wales and Newfoundland were originally adjacent, according with the hypothesis of continental drift.

2. GEOLOGICAL SETTING*

During the Cambrian both south-eastern Newfoundland and Wales were the sites of elongated, intermittently sinking basins in which shallow-water (see later) generally muddy deposition marked the inception of the respective Acadian and Welsh Palaeozoic geosynclines. During the Lower and Middle Cambrian these geosynclines occurred not as single, continuous marine troughs, but in the embryonic form of a string of semi-isolated basins of deposition of which the S.E. Newfoundland and Harlech-St. Tudwal's basins were examples.

The Harlech-St. Tudwal's basin was situated close to the axis of maximum subsidence of the Welsh proto-geosyncline. This N.E.-S.W. axis was offset westwards from the central line of the geosyncline, precisely as in the Acadian geosyncline (Weeks 1954). In Newfoundland the basin axis also trended N.E.-S.W. (it later suffered an anticlockwise rotation of about 30° in the Upper Devonian - see Black 1964), and had direct faunal connections with present Cape Breton island, Nova Scotia and New Brunswick, eastern Massachusetts, Wales and S.E. Scandinavia (Hutchinson 1962). The co-existent and parallel miogeosyncline of N.W. Newfound-

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Note: all orientations given in this paper relate to present pole positions land, Gaspé, St. Lawrence, northern Scotland, S.E. Greenland and western Norway generally remained isolated from the Acadian and Welsh geosynclinal unit.

Whilst not at all essential to the validity of the conclusions given in this paper, the hypothesis of continental drift will be presumed in that it makes more credible some otherwise quite extraordinary structural, geochemical and faunal coincidences. The statistically computed 'best-fit' of the continental margins of N. America, Greenland and N.W. Europe results in S.E. Newfoundland being placed to the immediate south-west of Wales (Bullard et al. 1965), and with the Acadian and Welsh Palaeozoic structures being both parallel and on the same alignment (Figure 1.). This coincidence is reinforced by the temporal, lithological and geochemical natures of the manganese carbonate beds of Newfoundland and Wales, and by faunal similarities. Howell (1925, p.125), speaking of the Paradoxides faunas of Newfoundland and central England, states: "not only are most of the species of these two widely separated regions the same, but their ranges are very nearly the same. Such a correspondence as this has probably seldom been equalled in all geological time". And Matley & Wilson (1946, p.27) state: "there is so remarkable a similarity between the fauna of the Newfoundland Cambrian and that of England and Wales, that many of the species are identical". Compelling geochronological evidence for an original proximity of N. America and Europe has recently been provided by Miller (1965), and, from preliminary palaeontological studies on Cretaceous sediments in the North Atlantic, by Funnell (1964).

Although the manganiferous horizons of S.E. Newfoundland and North Wales were formed pene-contemporaneously at the base of the Middle Cambrian (Hutchinson 1962, Mohr 1964), they lie within geosynclinal sediments of rather differing lithologies:

	Harlech Dome, N. Wales		S.E. Newfoundland	
Middle Cambrian	Gamlan Shales			
	Barmouth Grits	100-180m	Manuels River fm.	20-35m
	Manganese Shales (2m manganiferous horizons - the Ore Group - 10m above base.)	110-300m	Chamberlain's Brook fm. (1½m manganiferous beds in basal 3-5m.)	c.75m
Lower Cambrian	Rhinog Grits	350-750m	Brigus fm.	20-225m
	Llanbedr Slates	100-220m	Smith Point fm.	0-15m
	Dolwen Grits (base not seen)	120-150m+	Bonavista fm. (unconformable on Precambrian)	140m

The above table, which is not a correlation table, shows a contrast of alternating thick, very coarse or rather fine greywackes in North Wales with the thin variegated shales and slates of S.E. Newfoundland. Evidently the rate of sedimentation was much higher in North Wales, and in this respect the lithology of the Cambrian sediments of S.E. Newfoundland compares more closely with those of South Wales, where however a manganiferous basal Middle Cambrian horizon is lacking for reasons given below. Hutchinson (1962, p.21) has correlated the Chamberlain's Brook formation with the Solva Series in South Wales, and with the Trout Brook formation (Cape Breton island), the Fossil Brook formation (New Brunswick), and the Braintree formation (Boston).

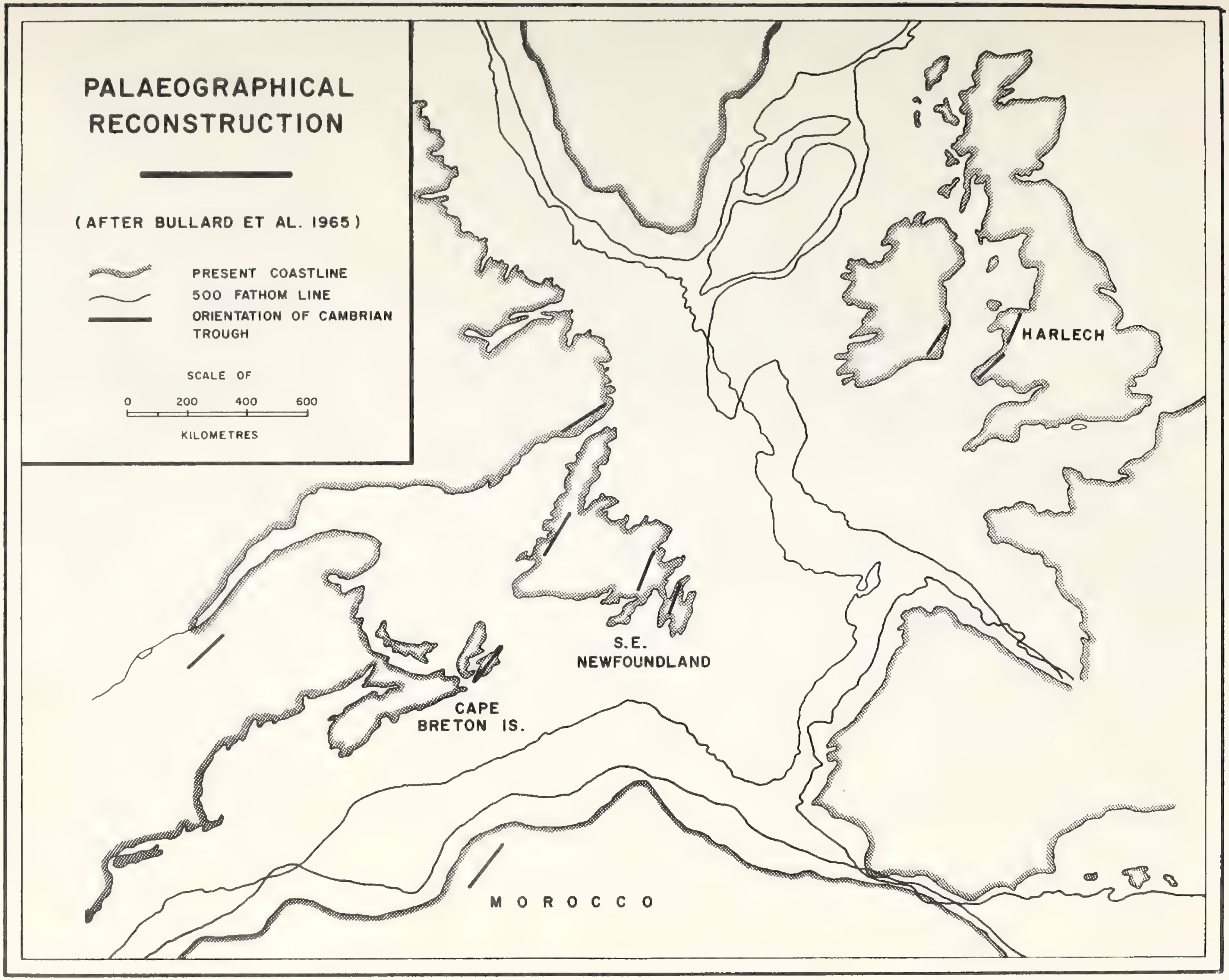
PALAEOGRAPHICAL RECONSTRUCTION
(AFTER BULLARD ET AL. 1965)
PRESENT COASTLINE
500 FATHOM LINE
ORIENTATION OF CAMBRIAN TROUGH
SCALE OF
0
200
400
600
KILOMETRES
HARLECH
S.E. NEWFOUNDLAND
CAPE BRETON IS.
MOROCCO

FIGURE 1

The Lower and Middle Cambrian sediments of the British Isles show rapid variations from one localised basin to the next, such that detailed correlations are often extremely difficult, despite the overall resemblances of which Jones (1955) writes: "the sequence of the Cambrian rocks in North Wales and in the St. David's district of South Wales are .... so similar that there is no doubt that the rocks in both areas were formed under closely comparable conditions". By contrast the Cambrian sediments of the Acadian geosyncline are regionally more uniform in their finer-grained lithology compared with those of Britain, bear a relatively prolific trilobite fauna, and largely escaped the effects of the Caledonian metamorphism which thus facilitates correlations.

Except for the closely associated manganese bed at St. Tudwal's the Ore-group sediments of the Harlech Dome are chemically unique in the Cambrian of the British Isles. The chemical relations of the Ore-group within the Manganese Shale Group have been discussed previously (Mohr 1956, 1959, 1964): essentially the Ore-group can be described chemically as merely Manganese shale diluted with a large quantity of manganese carbonate. The sudden single influx of the manganiferous solutions coincided with a temporary cessation of detrital sedimentation. In S.E. Newfoundland, at least two major manganiferous horizons and several minor ones occur within the basal 5m. of red shales of the Chamberlain's Brook formation (see Dale 1915); in this region the manganiferous solutions evidently reached or were precipitated from the basin of deposition in several pulses. Both in North Wales and S.E. Newfoundland the manganiferous beds are regionally restricted to areas of about 500-800 sq.kms.

Detailed petrographic and petrological descriptions of the manganiferous beds of Wales have been given by Woodland (1938, 1939) and Mohr (1964), and for those of S.E. Newfoundland by Dale (1915). These two occurrences of extremely fine-grained, banded rhodochrosite-silica rocks differ most in that those of Newfoundland were not subject to sufficiently strong Caledonian metamorphism for spessartine (and occasionally rhodonite) to abundantly develop, as was the case within the Welsh rocks.

3. DIRECTION OF THE SOURCE OF SEDIMENTS

The origin of the Lower and Middle Cambrian sediments which enclose the manganiferous beds has been better studied in Wales than in Newfoundland, and for the former region a comprehensive summary may be found in Bassett (1963).

The work of Bassett & Walton (1960) and Crimes & Sly (1964) on the Lower Cambrian Hell's Mouth Grits and Mulfran Beds of St. Tudwal's Peninsula, North Wales, has supported the conclusions of many previous workers that the source of detritus for these and the Harlech Grits Series was a northerly one, or more specifically a probable north-easterly one. Knill (in Bassett & Walton) considers that axial flow of turbidite sediments from the north-east took place along the N.E.-S.W. oriented Lower-Middle Cambrian geosyncline in North Wales, with the thick Llanberis Slate sequence of the Snowdonia district representing a marginal facies at the northerly end of the trough. However, evidence for an opposite direction of flow along the trough is found in the Barmouth Grits (Knill, op.cit.) and in the Upper Cambrian Maentwrog and Ffestiniog beds of North Wales (Evans, Garrett & Whitaker, 1966), in both cases sediments having entered from the south-west.

An axial orientation for the trough of N.E.-S.W. is confirmed by the lithology of the Manganese Ore of the Harlech Dome, where marginal facies of this horizon at Harlech in the north-west, and at Afon Gamlan in the south-east, are enriched in calcium relative to manganese, bear some detrital bands, and lack the typical tripartite Ore-group succession (Mohr 1955, 1964). At both these localities a close approach to margins of the basin of deposition is evident, though in view of the almost certain connection of the St. Tudwal's region to the Harlech basin the apparent north-western margin at Harlech must have been a local one. (This presumes no post-Cambrian tectonic displacement of St. Tudwal's relative to the Harlech region. There is tentative evidence that, relative to the present Harlech Dome, the St. Tudwal's region was displaced by Caledonian wrench faults and folding from a more north-westerly position to its present westerly one - Dr. W.E. Tremlett, personal communication).

The direction of the source of sediments for the Lower and Middle Cambrian horizons of Newfoundland is less certainly known, but the work of Weeks (1954) on sediments of the same age on Cape Breton island suggests a northerly or north-westerly lateral source, as opposed to the axial supply postulated above for the sediments of the Welsh geosyncline. However, Crimes & Sly (1964) have emphasised the complexity of Cambrian palaeocurrent directions in Wales, and the consequent need for caution in their interpretation until more extensive regional data are available.

4. SOURCE OF THE MANGANESE

(a) Introductory

Whilst the source of detritus in the Harlech Grits Series was probably north-easterly, the work of the writer (Mohr 1956, 1959, 1964) has suggested that the manganiferous solutions had a westerly origin, or more specifically a possible north-westerly one. If the Ore-group of the Harlech Dome is considered as a manganese-diluted Manganese Shale (Mohr 1964), calculation easily shows the greater manganese enrichment of the St. Tudwal's manganese bed relative to the enclosing Mulfran Bed silts compared with the Ore-group and Manganese Shale Group. As the St. Tudwal's manganese bed is also more thickly developed than the Ore-group of the Harlech Dome, and furthermore bears detritus such as is completely lacking in the lower part at least of the Ore-group, a westerly derivation of the manganiferous solutions seems strongly probable.

Separate directions of the sources of the detritus and the manganese in the Welsh rocks suggest that the manganese had some specific concentrated origin, rather than resulting from widespread weathering of the source-rocks of the detritus with a concomittant regional derivation of the manganese. The thesis of such a specific origin is supported by certain coincidences discussed below. It is therefore pertinent to consider what source, fitting with the regional lithological and palaeogeographical facts, could have suddenly provided the thirty million tons of manganese precipitated as twelve per cent by weight of the Ore-group sediments of the Harlech basin.

The source of the manganese became abruptly available with the commencement of Manganese Shale Group times, when there was an enrichment in manganese of about ten times over the earlier fine-grained sediments of the Llanbedr Slate. A further enrichment in manganese of about ten times, to form the Ore-group (Mohr 1964), coincided with a temporary cessation of detrital-hydrolysate sedimentation, but normal Manganese shale deposition was soon resumed. The next fine-grained formation above the Manganese Shale Group, the Gamlan shales, occasionally shows thin bands rich in spessartine, indicating that whilst appearance of the manganiferous source was abrupt, its termination was more gradual. This pattern is paralleled for the pene-contemporaneous manganese beds of S.E. Newfoundland (Howell 1925).

The remarkable enrichment of manganese in the Ore-group sediments was peculiarly unaccompanied by any comparable enrichments of any other elements, though there was slight enrichment in zirconium, cobalt and iron (Mohr 1964). Thus the ratio Mn/Fe in the Llanbedr Slate closely corresponds to that in igneous rocks at 0.02, but rises to 0.2 in the Manganese Shale and to nearly 2.0 in the Ore-group. In the St. Tudwal's manganese bed, considered to have been precipitated in between the Harlech basin and the manganiferous source, Mn/Fe reaches its peak at 3.65. This enormous enrichment of manganese relative to iron can next be considered as whether due to a primary enrichment at the source itself or to secondary enrichment during transport of solutions, or both.

(b) Possibility of a primary source

A primary source could have been one of two types (restricting the argument according to the uniformitarian hypothesis): either exposures of pre-existing specifically manganese-rich rocks made available to attack by weathering, or the contemporaneous eruption at surface of manganiferous volcanic rocks or hydrothermal solutions.

The former alternative would seem to be ruled out by the available field evidence regarding the Precambrian rocks of North Wales. Both Woodland (in Matley & Wilson 1946) and Bassett & Walton (1960) consider, upon the evidence of the petrography of the grits, that the source rocks fringing the North Wales Cambrian geosyncline were of Mona Complex type (Greenly 1919), though with greater exposure of spilitic, trachytic and keratophyric lavas and tuffs at the expense of silicic gneisses compared with the present-day exposures on Anglesey (Môna). Greenly in fact considered the Mona Complex rocks to be deficient in manganese, though greater expanses of such rocks as spilites and keratophyres would significantly (see later) have been favourable to a primary source-enrichment of manganese relative to iron. Nevertheless the evidence is not sufficiently compelling nor adequate to warrant postulating a sudden availability of exposures of pre-existing manganiferous rocks at the commencement of Manganese Shale times.

Park (1946) has demonstrated that the high concentration of manganese oxides in the Cretaceous spilitic sequence of Washington, U.S.A., probably owes to a contemporaneous separation and precipitation of manganese from the erupting and initially ferride-rich lavas. Krauskopf (1957) has presented theoretical evidence for such behaviour. H. Williams (1927) and D. Williams (1930) consider that the manganiferous tuffs of the Snowdon Ordovician volcanic province owe their origin to an initially high manganese concentration in the associated soda-rhyolites and keratophyres, and a similar origin for the spilite-associated Precambrian manganese ores of northern Sweden has been claimed by Odman (1947). The occasional genesis of abundant and pure manganiferous mineralisation in soda-rich volcanic provinces is an association which is becoming increasingly recognised, whether the eruption of these alkaline lavas be shallow-marine (Bouladon & Jouravsky 1956, Aguirre & Mehech 1964) or continental (Aguirre & Mehech op.cit., Mohr 1960).

There is no evidence for any contemporaneous submarine or continental volcanic activity during the greywacke deposition of the Lower-Middle Cambrian geosyncline in North Wales, excepting the spilitic rock within the Upper Manganese Shales at Diphwys (Mohr 1962). The presence of fresh spilitic detritus within these greywackes, however, prompts further enquiry in this direction, with attention now given also to the Acadian geosyncline.

The stratigraphy and palaeogeography of the Acadian geosyncline have been studied by Hutchinson (1952, 1956, 1962) and Weeks (1954) who have emphasised its essential miogeosynclinal character during the Cambrian, though by contrast with the parallel St. Lawrence-N. Scotland-W. Norway miogeosyncline there was eugeosynclinal development during the Ordovician in both Acadia and Wales. In S.E. Newfoundland two thin volcanic horizons are locally known in the Cambrian sequence: a thin breccia about sixty metres above the manganese bed, and a thin group of andesitic pillow lavas in the upper Middle Cambrian (Hutchinson 1962), either or both of which could well correspond with the Diphwys spilitic rock. Evidently, however, these posterior lavas cannot themselves have provided a manganiferous source for the earlier basal Middle Cambrian manganese beds of Newfoundland and Wales, despite the possibility that the lavas could have been spatially and even genetically related to such a source.

On present-day Cape Breton island, 400kms. to the south-west of S.E. Newfoundland, an important early Middle Cambrian volcanic centre was situated at the immediate north-west margin of the Acadian geosyncline, into which it provided both weathered debris and actual lava flows. Weeks (1954) has shown that much spilitic debris was incorporated in the greywackes deposited along the western, more rapidly subsiding side of the geosyncline, contemporaneous with more stable shelf-type muds to the east. No manganiferous sediments are known within the greywackes and lavas of this part of the Acadian geosyncline, however, and the relation of spilitic flows and detritus to manganiferous precipitation remains as tantalising as ever. A partial answer may lie in the necessity of an isolated body of alkaline water for large-scale manganese concentration and precipitation to occur (see below).

In his study of the "Cambro-Silurian" sedimentary iron-manganese ores of northern Norway, Foslie (1949) has shown that these deposits bear no direct relation to spilitic lavas, and where, further east, contemporaneous lavas of this type become abundant there are no locally associated ferride deposits. Similarly, the ferro-manganiferous calcareous sediments at the very top of the Lower Cambrian of central Poland are not related in any known way to the basic pillow lavas of the Cambrian Kaczawa eugeosyncline (Samsonowicz 1956). On the other hand, Bouladon & Jouravsky (1956) consider that the "Lower Infra-Cambrian" manganese deposits of Morocco (situated closely along the alignment of the Welsh-Acadian geosyncline prior to continental drift - Figure 1.) were precipitated at the end of a period of intense volcanism, with manganiferous hydrothermal solutions emanating from faults at the borders of the now meridionally orientated basins. These solutions were derived from the magma supplying the sodic rhyolites and ignimbrites, and veins within these rocks evidence a complete separation of manganese from iron. The same relation of manganiferous deposition to Infra-Cambrian alkaline silicic lavas and tuffs is observed in Algeria (Lucas 1956), and in both regions the hydrothermal source of the manganese is confirmed by the abundant presence of such elements as Ba, Pb, As and F. Hydrothermal veins composed almost entirely of massive spessartine, with accessory quartz, green hornblende, fluorapatite and tourmaline, have been described by Jonas (1942) from the Precambrian of S.W. Virginia, though a Caledonian age is ascribed by Jonas to this mineralisation.

Considering the interest of the N.W. African region to the present discussion, using the continental reconstruction of Bullard et al. (1965), it may be noted that no manganese deposits from the Lower-Middle Cambrian boundary are yet known there (Choubert - personal communication). More significantly, perhaps, thick tuffs occur near the top of the Lower Cambrian in the northern Anti-Atlas region, and spilites in the basal Middle Cambrian (Choubert & Faure-Muret 1956, and personal communication). This volcanic activity near the Lower-Middle Cambrian junction was accompanied by important tectonic uplift and emersion. Unconformities or peculiar lithology characterise the Lower-Middle Cambrian boundary over much of Europe and eastern N. America, features which are expanded on in a later section of this paper.

So it can be said that whilst a primary source for the manganese, either from volcanic emanations or the weathering of alkaline lavas, is particularly favourable to abrupt supply of very large quantities of this element in solution (compared with secondary processes of separation of manganese from iron, discussed below), the sedimentary manganese beds of the world show a variable relationship, spatially and temporally, to such primary source rocks (see Varentsov 1964). In the particular case of the basal Middle Cambrian manganese beds of Newfoundland and Wales no strictly contemporaneous lavas are found in present-day exposures closer than Cape Breton island, though further south along the geosyncline, in present-day N.W. Africa, the quantity of spilitic lavas greatly increases. Neither do the Newfoundland and Welsh manganese beds contain the great enrichments of trace elements commonly associated with manganese oxidate sediments, except that barytes is abundant at some horizons of the Newfoundland bed (Dale 1915). Whether this lack of trace element concentration is due to the form of manganous transport and precipitation, or to a peculiar type of source enriched only in manganese, remains to be elucidated, but the work of Mohr (1964) definitely favours the latter hypothesis.

In summary, direct evidence for a primary source of manganese, separated from iron, is lacking for the Welsh and Newfoundland Cambrian manganese carbonate beds. Nevertheless, various indirect factors favour such a source: its sudden availability, the remarkable purity of the manganese enrichment, the abundance of fresh spilitic and keratophyric debris in the greywackes of the Welsh geosyncline comparable with that found in the Cape Breton sediments where a contemporaneous volcanic source is proven, and the analogy of other sedimentary manganese deposits of high concentration within a very limited vertical extent, whose primary source is definitely established. If the source was to be ascribable to hydrothermal volcanic solutions, as in the case of the N.W. African deposits, then evidence of its existence will now be difficult to find except where associated lavas were occasionally extruded. Varentsov (1964) considers that manganese deposits associated with "greenstone" lavas bear higher amounts of trace elements than normal. More evidence is needed to confirm this statement, which applies to oxidates rather than to carbonate deposits, but even so trace element concentrations will reflect also the manner and distance of intervening transport between source and deposition.

(c) Possibility of a secondary source

Krauskopf (1957) considers that little preferential concentration of manganese over iron can occur during the weathering of rocks, though his rather limited data confirm those of Savage (1936) in showing that carbonic acid is a weathering agent with some bias to extraction of manganese in preference to iron, resulting in a higher Mn/Fe ratio in solution than in the parent rock. Source-rocks already bearing a relatively high Mn/Fe ratio, such as spilitic and keratophyric lavas, could further contribute to a high proportion of manganese in the weathering solutions, though it is most unlikely that in this manner the concentration of manganese could even rise to equal that of iron.

Secondary enrichment of manganese relative to iron during transportation is more definitely evidenced than during weathering. The greater ease of oxidation and precipitation of Fe^{++} relative to Mn^{++} ensures a tendency to separation, with the more stable Mn^{++} ion being the further transported from the source, and this separation can be enhanced by re-solution of any precipitated manganese with its further ensuing transport.

Krauskopf (1957) shows that precipitation of manganese from normal, oxygenated waters is only possible when the pH rises above 8, and that this fact could account for the local separation of manganese from iron described by Park (1946) in the Cretaceous spilites of Washington. pH values of over 8 are not often realised in large bodies of natural waters, but if concentration of waters took place in an isolated basin subject to strong evaporation than increased alkalinity would be possible. Iron hydroxide would be precipitated first, followed by manganous hydroxide which oxidises rapidly to manganese oxide. Krauskopf considers that this process of separation of iron from manganese during precipitation would be even more effective in the presence of slightly greater amounts of manganese than normal, and would also be facilitated by possible bacterial agencies and in the presence of large concentrations of silicate and carbonate ions.

Krauskopf sums up the problem of iron-impoverished manganiferous sediments, encircled by source rocks bearing no abnormal concentrations of manganese, stating (op.cit. p.77): "Probably the most essential requirement for accumulation of manganese from ordinary surface waters is that necessary slightly unusual conditions persist for a geologically long time". (author's emphasis). What any such unusual conditions might have been which could have operated for the formation of the Welsh and Newfoundland manganese beds, will be discussed in the next section. But it may be noted that secondary enrichment of manganese relative to iron in the processes of weathering, transportation and precipitation, whilst theoretically well established, requires the existence somewhere between the source rocks and the manganese deposits of correspondingly greater iron deposits. No contemporaneous ferriferous sediments are known for either the Welsh or the Newfoundland manganese beds. Furthermore the enrichment of manganese from the Llanbedr Slate through the Manganese Shale to the Ore-group is a hundred-fold, yet it is not accompanied by comparably large enrichments of any other element whatsoever (Mohr 1964). The purity of this enrichment does not seem conducive to the secondary enrichment theory, despite Varentsov's (1964) preference for this theory over that of a primary volcanic origin for the manganese of sedimentary manganese ores. Indeed, the fact cited by Varentsov that neither trace elements nor other major elements are generally enriched in sedimentary manganese carbonate ores only points to an unexplained and extraordinarily singular behaviour on the part of manganese itself in exogenetic processes. The writer, on the basis of detailed chemical studies (Mohr 1964), prefers to account for such singularity as due to a concentrated source rather than to severe weathering processes on normal rocks alone.

(d) The Climatic factor

In the particular case of the Welsh manganese carbonate bed, situated within a Precambrian provenance of rocks abnormally poor in manganese, the commencement of increased manganese influx into an isolated, carbonate-rich basin of precipitation was an abrupt one coinciding with cessation of detrital and hydrolysate sedimentation. This coincidence is too great to be dissociated from a consideration of the source of the manganese. The occurrence of the Ore-group within thick monotonously uniform shales, together with the geochemical affinity of the Ore-group to a manganese carbonate-diluted Manganese shale, makes it improbable that the temporary change in lithology had a purely tectonic cause; for example that the source region was lowered and then shortly afterwards uplifted again. More feasible, and supported by widespread indirect evidence, is that temporary, very unusual weathering conditions operated at the source during Ore-group times, thus relating manganese influx to the marked lithological change.

Woodland (1939) considers that the extremely finely dispersed silica and alumina now bound up in the Welsh Manganese Ore were derived from "the normal disintegration of a largely gneissic landmass", and with the manganese itself derived from the normal weathering of these pre-existing rocks. Geochemical evidence unfavourable to such an origin for the manganese has already been presented above, and by Mohr (1964). In discussing the formation of the Czechoslovakian Oligocene manganese deposits, Konta (1951) considers the presence of colloidal silica to indicate intense lateritic weathering conditions on land. Vologdin (1943) and Mikhalev (1946) consider that a hot climate with intensive weathering operated during formation of the basal Middle Cambrian manganese carbonate deposits of western Siberia. Thus in Kazakhstan bauxite beds are intercalated with the manganese, iron and phosphate deposits, suggesting not only intensive weathering but also the close proximity of the source rocks to the localised basins of deposition. Certain of the gondites of Madhya Pradesh, India, are considered by Straczek et al. (1956) to be of sedimentary origin, formed during a period marked by highly aluminous sedimentation; the precipitation of manganese coincided with temporary, restricted changes in nature and rate of clastic sedimentation, the manganese beds being associated with feldspathic clastics within a thick sequence of normal argillaceous sediments: again, abnormal weathering conditions at source are suggested. Indeed, Servant (1956) has observed the present-day formation of surficial crusts of manganese oxide, concentrated upon soils overlying manganiferous tuffs, under conditions of intense tropical lateritisation, though in the form of such oxides manganese tends to remain strongly fixed unless leaching solutions have a pH below 4 (Dakshinamurti & Mital 1961).

The geochemical evidence has shown that during Ore-group times intensive weathering conditions must have operated in the Welsh region such that there was a complete chemical breakdown of the source rocks to yield solutions of overall composition equivalent to those carrying much detritus during Manganese shale deposition (Mohr 1964). The increase in the precipitation of Ca, Sr and Na in Ore-group times was considered to reflect less the composition of the incoming solutions than the result of temporary isolation of the marine basin of precipitation, though the enrichment of the manganophile Co, and also of Zr, was probably related to the postulated intense weathering conditions which enabled the manganese concentration to occur.

Other evidence for abnormal climatic conditions during the Lower-Middle Cambrian transition in Britain is the presence of a peculiar, thin phosphatic band lying upon a slightly folded and eroded surface of the end-Lower Cambrian Lapworthella Limestone in Shropshire (Cobbold & Pocock 1934). The Lapworthella Limestone locally bears nodules enriched in manganese, phosphate and bituminous matter. In South Wales an unconformity marks the base of the Middle Cambrian Solva Series though without any evidence of manganese precipitation owing, perhaps, to a completely open marine environment in which salts could not concentrate. In the Cambrian strata of Warwickshire a pyrolusite-limonite-phosphate association occurs in the basal beds of the Abbey Shales which are dated by a Paradoxides aurora fauna as being of upper Middle Cambrian age (Illing 1916). In central Poland the sole calcareous horizon of the entire Cambrian in this region occurs at the very top of the Lower Cambrian, and is characterised by a high content of bituminous matter together with nodules of manganese-rich oxides (Samsonowicz 1956). Hayes & Howell (1937) have advanced several hypotheses to account for the presence of the peculiar, thin, shallow-water Black Limestone formation at the base of the Middle Cambrian in New Brunswick, though abnormal climatic conditions on land is not one of them; they prefer to account for the temporary cessation of detrital influx as due to tectonic factors. Vologdin (1943) notes the presence of evaporites associated with the western Siberian manganese deposits as evidence of a very arid climate in the Lower-Middle Cambrian. Varentsov (1964) considers that a severe, arid type of weathering occurred at source during formation of the great manganese deposits of the U.S.S.R., for example those of Usinsk and Nikopol.

The absence of either comparable or any manganese concentrations in the Cambrian strata elsewhere in eastern Canada or Britain than S.E. Newfoundland and the Harlech-St. Tudwal's basin was due, according to the above evidence, not to localisation of the postulated intense weathering conditions at the Lower-Middle Cambrian transition, but to localisation of suitable temporarily isolated basins of water for concentration and precipitation of salts to occur. The initial stages of transgression of the Palaeozoic seas favoured such localised conditions (Woodland 1939, Vologdin 1943, Vincienne 1956), as evidenced by the very variable lithology and thickness of sediments along the westerly displaced axis of the Acadian-Welsh geosyncline compared with the more stable shelf sea to the east. Thus Hutchinson (1962) notes that the Newfoundland manganese bed marked the disconformable commencement of Middle Cambrian sedimentation in a very restricted and localised basin, a basin which in fact was of very similar size to that of Harlech-St. Tudwal.

(e) Conclusions

There is at present no cogent evidence for the source of the manganese now contained near the base of the Newfoundland and Welsh Middle Cambrian shales. However, the arguments discussed in this paper strongly suggest a three-fold coincidence in the provision and concentration of this manganese:

1. The exposure at source of significantly manganiferous spilites and/or keratophyric lavas. The age of these lavas may have been Precambrian, Lower Cambrian, or most probably contemporaneous. Although no such contemporaneous lavas are known from the Welsh sector of the geosyncline (neglecting the Diphwys spilitic rock), they occur abundantly south-west of Newfoundland and (originally further south still) in Morocco. Manganiferous lavas are directly associated with "Infra-Cambrian" manganese beds in N.W. Africa, and more distantly so for the Lower-Middle Cambrian manganese beds of Poland and western Siberia. Directly manganiferous volcanic emanations are in significant quantities not postulated, as these would reduce the importance of factor 2. beyond what is in fact observed.

Secondary enrichment of manganese relative to iron, within weathering solutions derived from source-rocks bearing no abnormal quantities of manganese, is considered an inadequate process to have provided such an enormous and yet pure concentration of manganese over a brief period, and there is no evidence of contemporaneous precipitation of even comparable amounts of iron.

Thus the postulated source of the manganese concurs with that described by Shatskiy (1964) for his "volcanogenic-sedimentary" manganiferous formations: spilitic, keratophyric and "greenstone" lavas associated with siliceous sedimentation in local downwarps within a geosyncline. Shatskiy shows that the spatial and temporal relationships of these lavas to the associated manganiferous deposits may be very variable within the geosynclinal environment and its evolution.

2. Severe weathering conditions of a fluctuating, but generally rather hot and arid type at source. There is evidence that such a climate particularly marked the Lower-Middle Cambrian transition in eastern N. America and Europe (part of a postulated single continent at that time), though the presence in western Siberia of Lower Cambrian evaporites indicates that the period of hot aridity there was more extended.

Therefore factors 1. and 2. respectively provided a primary source for the manganese and its extraction by means of total decomposition of this source-rock. The postulated severe weathering conditions enabled a separation of the elements derived from the decomposed source-rock, according to the relative solubilities of ions under hot and frequently dessicating conditions (where iron is notoriously insoluble).

3. An isolated basin of precipitation in which the manganiferous solutions were able to concentrate. A basin totally or even largely enclosed by land is not necessarily required; solely that the bottom-waters of the basin were isolated by lack of circulation in completely stagnant conditions. The colloidal structures, persisting banding, and the unoxidised nature of the Welsh and Newfoundland manganese beds attest to these stagnant conditions. It will be shown that the basin waters were fully marine, in the next section of this paper.

Factor 2. may well have assisted in isolating the shallower of the many partially separate basins of deposition of the Middle Cambrian Acadian-Welsh geosyncline, through strong evaporation and virtual cessation of major river inflow.

Where any one of these factors was lacking there was no precipitation of manganese carbonate in the geosyncline. Open, circulating waters are held to account for the absence of a manganiferous horizon in South Wales and Cape Breton island, for example, and the absence of manganiferous lavas and/or severe arid climatic conditions for the vertical restriction within the Cambrian of the Acadian-Welsh manganese beds. However, it may be noted that manganese carbonate beds occur in the Ordovician of Belgium (Fourmarier & Calembert 1941), and in the Silurian of the St. Lawrence miogeosyncline (Caley 1936, Hewett et al. 1956).

5. DEPTH AND SALINITY OF THE BASIN WATERS

Kuenen & Migliorini (1950) consider that the graded bedding observed in the Harlech Series grits had its origin in the flow of turbidity currents down the marginal slopes of the geosyncline, and was formed in relatively deep waters comparable with those of the oceanic continental slope. Whilst slump structures are not uncommon in the Manganese Shale Group, and are even occasionally found in the Ore-group, yet the very localisation of the Harlech basin in early Cambrian times from the basins of Snowdonia and South Wales would seem to preclude a great depth to the waters. Concurring with most previous workers, Bassett & Walton (1960, and ensuing discussion) show that the Hell's Mouth Grits immediately underlying the manganese bed at St. Tudwal's were deposited in quite shallow waters, and some horizons show evidence of deposition above wave-base. The presence of a trilobite fauna in intimate association with the manganese beds of S.E. Newfoundland is also indicative of a shallow-water environment.

It is therefore considered that the Ore-group sediments were precipitated in relatively shallow waters of some tens of metres rather than hundreds of metres depth, shallow enough to have been isolated and appreciably concentrated by strong surface evaporation, but not so shallow that atmospheric oxidation of bivalent iron and manganese was facilitated. In postulating an enclosed basin for the precipitation of the Newfoundland manganese bed, Dale (1915 p.444) states that "the early Cambrian sea of southeastern Newfoundland must have been of so restricted and shallow a character as to allow of a concentration of the manganese salts sufficient to form deposits of such dimensions and character as we now find". In fact the extent of the manganese beds within the S.E. Newfoundland basin was localised to 500-800 sq. kms. about the Trinity and Conception Bays region, an area of the same size as that of the Harlech basin. Mikhalev (1946) states: "We may now consider definitely established that the deposition of manganese ores proceeded in the near-shore sea basins, along the periphery of the weathering continents".

Considering Woodland's suggestion (1939 p.34) that the Welsh Manganese Ore was precipitated in fresh-water, and its reiteration by Stubblefield (1956) and others, it is necessary briefly to emphasise both the palaeogeographical setting and the geochemical evidence which militate against such a hypothesis. The isolated marine character of the Ore-group basin is consistent with the fully marine environment of the Harlech Grits Series as a whole (Matley & Wilson 1946, Bassett & Walton 1960), as well as concurring with the environment of formation of the manganese carbonate beds of western Siberia and Czechoslovakia, and does not require the very radical yet short-lived tectonic changes necessitated by a fresh-water environment. Furthermore, in the case of the S.E. Newfoundland manganese carbonate sediments, Hutchinson (1962) has discovered a trilobite fauna actually contained within them.

On geochemical grounds the writer (Mohr 1959) has shown the Manganese shales to have been deposited in a marine environment, and (1964) has confirmed this for the Ore-group through the remarkable geochemical relation of the Ore-group precipitates to the Manganese shales. Even allowing for appreciable "inherited" boron in the shale hydrolysates, the boron-vanadium discriminant function (Potter et al. 1963) yields fully marine values for both the Llanbedr Slate and Manganese Shale Groups. The lower B-V content of the Ore-group sediments is related to lack or paucity of hydrolysates and the dominance of the carbonate anion rather than to any marked decrease in salinity. Indeed, the concentration of silica, alumina and metal ions required to precipitate and form the Manganese Ore gel presupposes an incidental increase in salinity in strongly evaporating waters of the temporarily isolated basin. The close association of halite deposits with the Middle Cambrian manganese carbonate beds of western Siberia cited by Vologdin (1943) has already been remarked on.

Within the isolated, stagnant, alkaline marine basins of S.E. Newfoundland and Harlech-St. Tudwal's, the existence of the shallow sea-bottom within the zone of saturation permitted the precipitation of the manganese carbonate. This precipitation seems most likely to have been confined to physico-chemical processes consequent on saturation, rather than some unknown and unevidenced biochemical process. The saturation of the basin waters owed to two factors: (i) concentration of salts due to continued influx of metalliferous solutions, and (ii) concentration of salts due to strong evaporation from the isolated basin waters. There is some evidence (Mohr 1964) that the Ore-group was derived from a single, initial influx of manganiferous solutions, there being little consequent influx during the arid climatic conditions of Ore-group times. Strong evaporation under these arid conditions would have assisted the temporary isolation of shallow, warm water basins. Vologdin (1943) estimates that an average temperature of at least 25°C operated during deposition of the Middle Cambrian manganese carbonate beds of western Siberia, and also for the associated thick evaporite deposits; Vologdin suggests that this high temperature may have intensified any biochemical processes of precipitation. Konta (1951) considers that the Czechoslovakian Oligocene manganese deposits formed by concentration of salts in isolated basins under tropical conditions, the waters of the basins becoming appreciably alkaline.

Therefore it can be concluded that at the commencement of the Middle Cambrian, solutions enriched in manganese entered the Acadian-Welsh proto-geosyncline and were concentrated in isolated marine basins over S.E. Newfoundland and Harlech-St. Tudwal's. In the latter region, slight but appreciable precipitation of manganese carbonate began during muddy, turbidite sedimentation, but at the commencement of Ore-group times the Harlech-St. Tudwal's basin became isolated from the open sea, and an enormous influx of manganese coincided with complete cessation of turbidite sedimentation. In the S.E. Newfoundland basin much finer-grained and slower muddy sedimentation was interrupted on two major occasions and a number of minor ones for the precipitation of manganese carbonate from clear, stagnant waters. In both regions the temporary isolation of the basin of deposition enabled concentrated flocculation and precipitation of colloids and salts from the saturated alkaline waters.

6. PHYSICO-CHEMICAL CONDITIONS OF THE WATERS OF PRECIPITATION

(a) Regional conditions

For the Welsh Ore-group the relation of iron to manganese precipitation has been briefly considered by Woodland (1939 p.27) who states that "immediately before the formation of the actual [manganese] ore band began, the waters contained considerable quantities of manganese in solution, together with a greater amount of iron than is represented in the composition of the ore band itself. Precipitation began under reducing conditions.... iron sulphide was thus precipitated while the bulk of the manganese remained in solution .... The manganese, with the rest of the iron, was then precipitated as carbonate".

The greater ease of precipitation of the Fe^{++} ion, especially in the presence of the sulphide ion, relative to the more stable Mn^{++} ion has long been established, and adequately explains the ubiquitous occurrence of the Pyritiferous Mudstone formation immediately beneath the Manganese Ore, except that the Mudstone is notably absent from the fringing S.E. and N.W. regions of the basin where current turbulence and mixing remained appreciable. These fringe conditions were exacerbated at St. Tudwal's, west of the Harlech basin, where uniform mixing of iron and manganese was fully obtained. Where the Pyritiferous Mudstone is ill-developed, as at Harlech and Afon Gamlan on the respective N.W. and S.E. fringes of the Harlech Dome region, the Manganese Ore has a low Mn/Ca ratio and is deplenished in iron, but the basal members of the overlying Bluestone formation often show a dispersed development of pyrite-chlorite layers, suggesting either a renewed minor influx of ferride-rich solutions or, more probably, further precipitation of incompletely deposited ions from the basin waters (Mohr 1964).

In the axial region of the Harlech basin where the Ore-group is most typically developed, the initial precipitation was one of iron sulphide, silica and ferrous hydroxide? . If the iron sulphide was colloidally precipitated through the agency of sulphide-reducing bacteria yet there was a remarkable lack of sorption of such elements as cobalt and nickel (Mohr 1960). Krumbein & Garrels (1952) consider that a pyritic sediment would be typically deposited in slightly alkaline waters (pH 7.0-7.8) and under reducing conditions (Eh -0.2 to -0.3). A slight increase in pH and/or Eh would allow of the formation of magnetite such as is commonly observed as a diagenetic mineral in the Pyritiferous Mudstone.

Following precipitation of the bulk of the iron, continuing strong evaporation from the stagnant basin-waters resulted in precipitation of manganese as carbonate, together with minor amounts of calcium, magnesium and iron, and appreciable quantities of silica and aluminium hydroxide. The waters of the basin would have been heavily charged with CO_2 as a result of precipitation of carbonates from bicarbonate solution, a factor assisting the non-oxidation of the manganous ion. Around the fringes of the basin, except at St. Tudwal's where there was passage of incoming manganiferous solutions, the ratio of precipitated $CaCO_3$ to $MnCO_3$ was greater owing to the relative stabilities of these two metal ions, but total (Mn +

Ca + Mg) remained virtually constant in the Ore sediment over the whole basin, also including the Newfoundland manganese deposit (Mohr 1956).

Although it is difficult to fix the precise pH-Eh conditions under which the Manganese Ore gel was precipitated, lacking any definite information on anionic abundances in the waters of precipitation, it has been approximately estimated by Krumbein & Garrels (1952) that the Newfoundland manganese bed was formed under a pH of 7.0-7.8 and an Eh of 0.0 to -0.2. These are conditions which could easily have overlapped with those for the Pyritiferous Mudstone, and indeed authigenic magnetite is found both in the Pyritiferous Mudstone and the Manganese Ore, though much less abundantly in the latter (Mohr 1963).

(b) The banding of the manganese beds

In a previous paper the writer (Mohr 1964) has shown that the sediments of the Ore-group were deposited at approximately the same rate as operated for the enclosing Manganese shales, and with the banding of the Ore and Bluestone of corresponding thickness to the bedding of these shales. Jones (1955) calculates that the average rate of deposition of the Harlech Series sediments was 130 years/cm. using 60m.yrs. as the duration of the Cambrian period: using the more recently established duration of 100m. yrs. for this period, a rate of 215 years/cm. is obtained. Even if allowance be made for unobserved and unsuspected non-sequences in the Harlech Series, it is unlikely that the rate of precipitation of the Ore-sediment could have been so rapid as to permit the seasonal origin of the banding that Woodland (1939 p.26) and Mohr (1956) suggested. Rather, the hypothesis of Wilson (1964), which accounts for the Pleistocene ice-ages and the Tertiary cyclothems as due to fluctuations of the Antarctic ice-sheet, could be more suitably applied to the banded manganese-iron deposits of the late Precambrian and early Palaeozoic.

Mohr & Allen (1965) have shown on geochemical grounds that the coloured banding of the manganese beds of Wales and Newfoundland represents precipitation through successive and cyclical changes of environmental conditions, rather than a post-depositional diffusion throughout an originally uniform and unbanded bed. Supporting evidence for an original banding includes the lateral persistence of individual bands at constant horizon, the diffusion within individual coloured bands according to the frequently sharply defined separation of silica-aluminous gel from carbonate gel, and the complete restriction of haematite to the red bands and of manganese oxide to the black bands when the mineralogy of the red, black (or green) and yellow bands is in each case distinguished by merely proportional differences of the same essential bulk minerals.

The crudely developed cyclical banding of these manganese beds is therefore considered to be derived from variations in the rate and type of precipitation according to changes in rate of evaporation from the basin-waters, and possibly in the rate of further influx of manganiferous solutions. The greater parts of the Manganese Ore and the Newfoundland manganese bed are composed of relatively thick, persistent bands of red material whose colouration is due to the presence of small amounts of haematite. The original precipitation of ferric hydroxide suggests that a higher Eh operated than during formation of the yellow and black bands where iron occurs predominantly in the ferrous state (Woodland 1939). The red bands are also marked by a higher spessartine/rhodochrosite ratio than the yellow and black bands (excepting the 'solid' garnet yellow spheroids), reflecting a higher proportion of silica and aluminium hydroxide compared with carbonate in the original precipitate. As silica and alumina are both amphoteric, their precipitation as hydroxides suggests a pH value close to 7.0, closer to neutral than the more alkaline pH which characterises the carbonate-rich precipitation of the yellow and black bands.

The postulation of slightly higher Eh and lower pH conditions for the red bands compared with the yellow-black bands in the Welsh Manganese Ore also helps to explain the distribution of various trace-elements, especially copper, between the coloured bands (Mohr 1956). However, the presence of manganese oxide in the black bands would seem not to accord with the lower Eh conditions postulated on the basis of dominant ferrous iron in the black and yellow bands compared with the red. The oxidation of the manganous ion proceeds less readily than that of the ferrous ion, but the anomaly remains that in the Manganese Ore haematite and manganese oxide are never found occurring together in the same band. Where ferric iron is high, manganese occurs wholly in the manganous state, and where manganese is present in traces in the quadrivalent state the iron occurs dominantly in the ferrous state and without any visible haematite. It is therefore evident that considerations of Eh alone are inadequate to explain the formation of the minute amounts of manganese oxide in the black bands, and notably without any trace element enrichments such as often mark the manganese oxidate sediments (compare the data of Mohr & Allen 1965 with Rankama & Sahama 1950).

Since ferric hydroxide starts to precipitate at a lower pH than manganese oxide at a given Eh (Krauskopf 1957), it is seen that Eh-pH relations are unable completely to explain the peculiar mineralogy of the Ore bands, and the presence of the manganese oxide characterising the black bands must be sought in other factors of which bacterial agency (Krauskopf 1957) and trace element catalysis (Lenher 1916) seem the most promising. Certainly the colourations from haematite and manganese oxide are most intense in the Ore from the original axial region of the Harlech basin where the Ore reaches its thickest development and where colloidal structures are most sharply preserved. This partial-oxidation colouration does not owe to post-depositional processes, for at Moelfre, where the Ore band colourations are particularly intense, the Pyritiferous Mudstone grades up into material of typical Ore aspect but with the colloidal banding transitionally coloured white and pale-green; only after about 6cms. of this transitional Ore material does the typically purple-red, black and yellow banded Ore develop. The indication is that manganese carbonate precipitation at Moelfre commenced prior to the higher Eh conditions which obtained for the typical Ore sediment.

No manganese oxide-bearing black bands are found in the Newfoundland manganese beds, but their precise correspondent takes the form of intensely green-coloured bands. It is known that these green bands show a great predominance of ferrous over ferric iron (Dale 1915), exactly as in the black bands of the Welsh Manganese Ore, but the mineralogical site of this ferrous iron remains to be elucidated.

banding of the Newfoundland and Welsh manganese beds. With a relatively cooler and less arid climate on land the volume of waters entering from the western margin of the Acadian-Welsh geosyncline would have become more appreciable, so aiding circulation of oxygenated currents as well as lowering dissolved CO_2 content. This slightly oxygenated dilution would have favoured oxidation of ferrous to ferric iron in the bottom precipitate, such as is now represented by the red bands. The dilution and/or relative lack of evaporation from the isolated basin waters caused a greater proportion of silica and aluminium hydroxide to precipitate relative to manganous carbonate, and this was aided by the dilution of alkalinity closer to neutral. The smaller amount of red material relative to yellow and black in the basal part of the Welsh Manganese Ore suggests control by: (i) deplenishment of the basin waters in iron, silica and alumina due to the preceding precipitation of the Pyritiferous Mudstone sediment, and (ii) relatively low Eh conditions persisting from the Pyritiferous Mudstone period.

(c) Conclusions

The basal Middle Cambrian manganese beds of the Acadian-Welsh geosyncline were formed in isolated stagnant marine basins, with precipitation of manganese carbonate being aided by strong surface evaporation. The waters were, shallow, warm, clear, alkaline and probably highly saline.

In the Welsh Harlech-St. Tudwal's basin there was partial separation of iron and manganese at the commencement of precipitation. The banding of the manganese beds was due to long-term climatic variations, which can be summarised as follows:

			characteristic form of			
Band	pH	Eh	Fe	Mn	CO_3/SiO_3	Climate
red	close to neutral	close to zero	Fe_2O_3,Fe_3O_4	$MnCO_3$	lower	long duration - cooler, less arid
yellow	alkaline	negative	$FeCO_3$	$MnCO_3$	highest	short duration - hot, arid
black or green	alkaline	negative	$FeCO_3$	MnO_2,$MnCO_3$	higher	

In the Welsh basin there was a gradual return to normal shale deposition through the Bluestone formation, haematite and manganese oxide now being absent, but with continuing alternating precipitation of carbonate-rich and silica-alumina-rich bands and with minor inclusion of very fine-grained detritus.

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